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*Mendeleev Commun.*, 2008, **18**, 59–61
Mendeleev Communications

# Volume of electrostriction of the solvate-separated ions of lithium perchlorate and contact ion pair of the transition state in sulfenyl insertion

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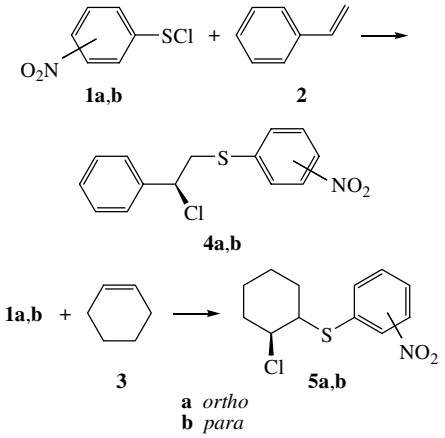
DOI: 10.1016/j.mencom.2008.01.022

The volumes of electrostriction of the ions of lithium perchlorate are in a linear relation with the solvent electrostriction parameter $\partial(1/\varepsilon)/\partial p$ but the volume changes of ion pair transition state of electrophilic addition of aryl sulfenyl chloride to styrene and cyclohexene have the slope about 20 times less.

The high pressure effect on the rate and equilibrium of chemical reactions is of interest in pure and applied chemistry.[1–5] The nonpolar Diels–Alder reaction is convenient to elucidate volume changes in the absence of electrostriction.[3,6–8] Large electronic and steric effects of substitutions, as well as a solvent effect on the rate of the Menshutkin reaction at ambient and elevated pressure, have been intensively studied.[5] Here the charge separation can only grow during this reaction. On the other hand, a lot of substitution or addition processes have nonpolar initial and final states but a polar transition state. The substitution and solvent effects can be a reason for the transformation from polar nature of the transition state to nearly nonpolar one.[9] Sulfonium ion pair type of transition state was proposed for the electrophilic addition of sulfenyl halides to alkenes.[10] This assumption follows from the large solvent effect on the reaction rate and stereoselective *trans*-addition with formation of β-halide thioether. The transformation of the transition state from polar to nonpolar was proposed[11] for this reaction, when polar-type stabilization sharply decreases on going from polar to nonpolar media.




**Scheme 1**

If a polar transition state of the reaction is the same in polar and nonpolar media, solvent electrostriction should be in all solvents. But in this case the volume of activation in nonpolar solvents (*n*-hexane, carbon tetrachloride) should be more negative than that in polar ones.[2,5] On the other hand, if the transition state of the reaction is polar in a polar solvent but has a nonpolar type in a nonpolar medium, solvent electrostriction should be lack in the last case and the volume of activation in a polar solvent should be more negative. A polar solvent effect on the activation volume of $Ad_E$ reaction (Scheme 1) was published recently.[12]

Lithium perchlorate with high solubility in organic *n*-donor solvents can be a suitable model of the ionic type of the transition state of chemical reactions. Solvent effect on the partial molar volume (PMV) of lithium perchlorate was measured for dilute solution.[13] The details of kinetic measurements under pressure were published elsewhere.[8,12] The rate constants of these reactions (Scheme 1) decrease in $10^6$ times on going from acetonitrile to *n*-hexane. Long monitoring time (20–50 h) of the optical density change for *p*-nitrophenyl sulfenyl chloride was necessary because of the very slow reaction of **1b** with styrene **2** in *n*-hexane at 25 °C. The obtained rate constants were $1.80\times10^{-5}$ at atmospheric pressure; $5.45\times10^{-5}$ at 530 kg cm$^{-2}$ and $1.16\times10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 960 kg cm$^{-2}$. From these data the apparent volume of activation in *n*-hexane was calculated as –49.3 cm$^3$ mol$^{-1}$.

$$-RT\left(\frac{\partial \ln k}{\partial p}\right)_T = \left(\frac{\partial G^{\neq}}{\partial p}\right)_T = \Delta V^{\neq}_{\text{exp}} \quad (1)$$

Because of the concentration of reagents (and the frequency of collision) growth under pressure due to the solvent compressibility, required correction for the second order reaction should be made.

$$RT\frac{\partial \ln k}{\partial V}\frac{\partial V}{\partial p} = \beta_T RT = -\Delta V^{\neq}_{\text{conc}} \quad (2)$$

The compressibility coefficient [$\beta_T = V^{-1}(\partial \text{V}/\partial \text{P})$] of *n*-hexane was measured in a special high pressure vessel up to 1000 bar at 20, 30, 40 and 50 °C. The Tait equation (3) has the best accuracy[2] in description of the $V_p$–$p$ dependences.

$$\Delta V/V_0 = C\ln[(B + p)/B] \quad (3)$$

The coefficients $C$, $B$ and $\beta_T$ were obtained as 0.088123, 548.50 and $160.66\times10^{-6}$ bar$^{-1}$ at 20 °C; 0.088342, 501.69 and $176.09\times10^{-6}$ bar$^{-1}$ at 30 °C; 0.087517, 451.62 and $193.78\times10^{-6}$ bar$^{-1}$ at 40 °C and 0.088855, 415.10 and $214.06\times10^{-6}$ bar$^{-1}$ at 50 °C. From obtained dependence: $\beta_T = 137.22 + 0.93015T + 0.012125T^2$ ($R = 0.999997$), the value of $\beta_{25}$ was calculated as $168.05\times10^{-6}$ bar$^{-1}$ at 25 °C. Using these data $\Delta V^{\neq}_{\text{conc}}$ [equation (2)] was calculated as –4.1 cm$^3$ mol$^{-1}$, and the corrected volume of activation ($\Delta V^{\neq}_{\text{exp}} - \Delta V^{\neq}_{\text{conc}}$) of the reaction (**1b** + **2**) in *n*-hexane at 25 °C was determined as –45.2 cm$^3$ mol$^{-1}$.